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with water in sonorous undulations, was found to be much greater than that upon the ear connected with the same water by means of a solid rod. When both tube and solid rod were employed simultaneously, sound was heard in that ear only supplied with the tube

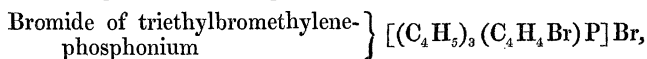
*February 24, 1859.*

Sir BENJAMIN C. BRODIE, Bart., President, in the Chair.

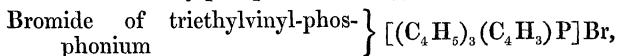
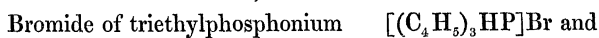
The following communications were read:—

- I. "Researches on the Phosphorus-Bases."—No. V. Diphosphonium - Compounds. By A. W. HOFMANN, LL.D., F.R.S., &c. Received January 20, 1859.

In a note\* on the department of dibromide of ethylene with triethylphosphine, I have stated that the reaction between these two substances gives rise to the production of



whilst two other bromides, viz.



are generated in consequence of secondary processes. But I did not fail to remark in the same note, that in addition there is formed in this reaction a fourth bromide, the nature of which, at that time, I had been unable to fix by experiment.

I have continued the study of this substance, which has led to the following results.

All attempts to eliminate the bromide in question by frequently recrystallizing the direct product of the action of dibromide of ethylene on triethylphosphine have entirely failed. Considerable sacrifice of precious material and often repeated analyses of the different crops of crystallization taught me nothing, except that the body

\* Proceedings, vol. ix. p. 287.

which I endeavoured to grasp is most abundantly produced when the triethylphosphine is rather in excess. Indeed, it would appear, that under those conditions, the bromide in question constitutes the principal product of the reaction.

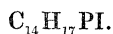
Not more successful was an attempt to increase the chances of separation by reducing the number of the bromides.

As I have previously stated, treatment with oxide of silver destroys the triethylated-bromethylene-phosphonium, converting it into a basic compound, which contains no longer any bromine, whilst the same agent transforms the bromide of triethylphosphonium into the oxide of argento-triethylphosphonium, and the dioxide of triethylphosphine. On saturating again by hydrobromic acid the liquid thus produced, the solution now contained only the new bromide, the bromide of the debromineted body, and the dibromide of triethylphosphine, the extreme solubility of which rendered its presence almost harmless. The task was thus virtually reduced to the separation of two bromides. Unfortunately, the two substances resemble each other to such an extent, that this hope also had to be abandoned.

A modification, however, of this process led to the solution of the difficulty. On saturating the alkaline solution, produced by the action of oxide of silver upon the crude bromides, with hydriodic instead of hydrobromic acid, a mixture of the corresponding iodides was obtained, the separation of which could be easily accomplished.

On moderately concentrating this solution, a beautiful iodide of limited solubility was deposited. This substance readily dissolved in boiling water, from which it crystallized on cooling in long white needles. It was less soluble in alcohol, insoluble in ether.

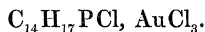
The analysis of this compound, carefully purified by repeated crystallizations, led to the following atomic expression:—



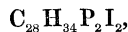
This formula received ample confirmation by the examination of a platinum- and gold-compound. Converted into chloride and precipitated by dichloride of platinum, the new body furnished a crystalline, difficultly-soluble platinum-salt, differing from the platinum-salts of all the other compounds of this group. This salt dissolves in boiling concentrated hydrochloric acid without decomposition, and crystallizes on cooling in beautiful yellow needles containing



The gold-salt is a bright yellow crystalline precipitate, difficultly soluble in boiling water, and not recrystallizable without some alteration. The gold-determination agreed with the formula



The preceding formulæ are simple translations of the analytical results, but they convey no idea regarding the nature of the new body. Legitimate interpretation of these expressions, and a due appreciation of the conditions in which the new compounds are formed, unavoidably lead us to the conclusion that the formulæ must be doubled. The molecule of the new iodide thus becomes



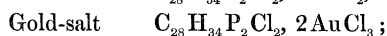
corresponding to an original bromide,



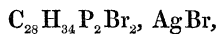
which is simply formed by the association of 2 equivalents of triethylphosphine and 1 equivalent of dibromide of ethylene,



The formulæ of the platinum-salt and of the gold-salt of course have likewise to be doubled :



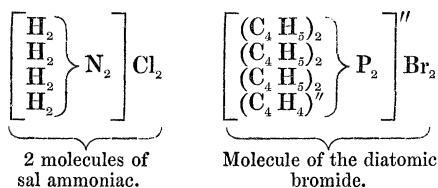
the number of platinum- and gold-equivalents which respectively exist in these compounds being apparently determined by the number of triethylphosphine-equivalents associated in the new salt. I have vainly endeavoured to produce compounds containing only one equivalent of platinum and gold, but have succeeded in procuring a well-defined silver-compound :



which is formed by treating the new bromide with a quantity of oxide of silver insufficient for complete decomposition. This compound is a double salt of equal equivalents of the proximate constituents.

The department of triethylphosphine with dibromide of ethylene, and more particularly the formation of the new bromide, is not with-

out theoretical interest. The molecule of dibromide of ethylene, equivalent to 2 molecules of hydrobromic acid, fixes in this reaction 2 molecules of triethylphosphine, equivalent to 2 molecules of ammonia, the result being a compound saline molecule, equivalent to 2 molecules of sal ammoniac.



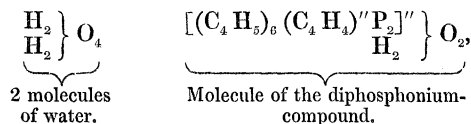
It is not quite easy to frame a name for this complex body, in which, under the influence of the diatomic ethylene, 2 molecules of triethylphosphine are, if I may say so, *dovetailed* together. We have in this case to deal with a compound molecularly representing 2 equivalents of chloride of ammonium, with phosphorus in the place of nitrogen, bromine in the place of chlorine, 6 equivalents of ethyl and 1 equivalent of diatomic ethylene being substituted for the 3 equivalents of hydrogen; in fact, the compound is a dibromide of hexethyl-ethylene-diphosphonium, *sit venia verbo*.

Those who have accorded some attention to the direction of these researches, cannot have failed to observe that the conception of the compound which forms the subject of this note was the point from which I started in examining the deportment of triethylphosphine with dibromide of ethylene. In a note on polyammonias, presented to the Royal Society about a year ago\*, I first pointed out the existence of similar compounds in the nitrogen-series, adducing in favour of this view such experimental evidence as I was enabled to collect from the materials at hand. I have since endeavoured to expand this evidence by the realization of a variety of bodies of analogous constitution. For this purpose I have examined the action of ammonia on dibromide of ethylene; a process, which, owing to the number of bodies simultaneously produced, presents considerable difficulties. With the view of simplifying the reaction, I have passed step by step to the primary, secondary, and tertiary monamines, in which the advancing state of substitution promised a reduction of the number of compounds capable of being generated under the influence of

\* Proceedings, vol. ix. p. 150.

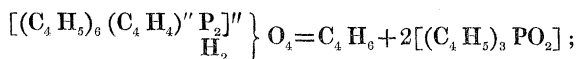
dibromide of ethylene. These experiments, some of which have been laid already before the Royal Society, whilst others are still incomplete, have furnished many additional illustrations of the group of polyammonias; but most of these reactions are complicated, and the compounds produced are far from always presenting the salient characters which I could have desired. In fact, it was not until I pursued the inquiry into the phosphorus-series, and relying on the promptness and precision with which these substances act, examined the deportment of dibromide of ethylene with triethylphosphine, that the experiments were attended by the desired success.

The new diphosphonium-compounds which form the subject of this note are remarkable for their well-defined characters, and for their stability. They may be heated to 250° C. without undergoing the slightest change. Even the dioxide, which is readily liberated by the action of oxide of silver upon either the bromide or the iodide, is a very stable compound. The solution of this substance, which obviously corresponds to 2 molecules of water,



is a powerfully alkaline liquid, attracting with great avidity the carbonic acid of the atmosphere, and precipitating the metallic oxides like potassa. The solution may be evaporated without change to a syrup-like liquid, and it is only at a very high temperature that decomposition actually takes places. At one time I had hoped to see this body splitting under the influence of heat into the ethylene-alcohol (glycol) and triethylphosphine, but the transformation ensues in another form, only traces of phosphorus-base being liberated, while the principal product is the dioxide of triethylphosphine, which, in the latter stages of the distillation, coats the neck of the retort with a network of beautiful needles; a small quantity of gas (hydride of ethyl?) being simultaneously evolved.

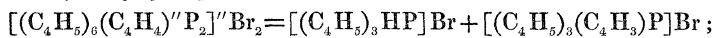
The reaction is probably



this equation, however, is not experimentally established.

The molecule of the diphosphonium-bromide contains the elements

of 1 molecule of bromide of triethylphosphonium and 1 molecule of triethyl-vinyl-phosphonium,



I have endeavoured to split the latter in accordance with the above equation, but without success.

Triethylphosphine acts with energy upon the homologues of dibromide of ethylene; I have not yet examined, however, any of the products thus obtained. Mr. W. Valentin, to whom I am indebted for much valuable assistance during my experiments, has found, moreover, that triethylarsine unites with dibromide of ethylene. He has not yet completed the investigation of the crystalline body which is generated in this reaction.

II. "On the Different Types in the Microscopic Structure of the Skeleton of Osseous Fishes." By A. KÖLLIKER, Professor of Anatomy and Physiology in the University of Würzburg. Communicated by Dr. SHARPEY, Sec.R.S. Received January 20, 1859.

After having been occupied for several months with observations on the minute structure of the bones of fishes, I now take the liberty to present the results of my studies to the Royal Society.

The principal fact which I have to mention is, *that a great many genera of osseous fishes possess no bone-corpuscles, radiated or fusiform, in their skeleton, and therefore no real osseous tissue.* That there exist fish-bones without bone-corpuscles must have been long known in England to those who have collections of microscopic preparations of the hard tissues of animals, as Owen, Tomes, Williamson, Quekett, and others; but nobody seems to have mentioned the fact before Williamson, Quekett, Dr. Mettenheimer of Frankfort, and myself\*. In the year 1850 Professor Williamson pointed out the absence of bone-corpuscles from the bones of the Cod, Haddock, Perch, Plaice, Pike, and various other fish, distinguishing them in

\* Since this communication was read to the Society, Dr. Sharpey has directed my attention to a statement by the late Professor J. Müller, to the effect that in the Pike and many other fish the bones are destitute of bone-corpuscles. This statement occurs in Müller's Annual Report of the progress of Anatomical and Physiological Science in 1835, and is repeated in his addition to the work of Miescher, "De Inflammatione Ossium, eorumque Anatome Generali," Berlin, 1836, p. 269.